A STUDY OF THE MECHANISM OF THE TITANIUM-LIQUID OXYGEN EXPLOSIVE REACTION

TECHNICAL REPORT ASD-TR-61-479

DIRECTORATE OF MATERIALS AND PROCESSES
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

PROJECT No. 7351, TASK No. 73521

(Prepared under Contract No. AF 33(616)-7595 by
Battelle Memorial Institute, Columbus, Ohio;
J. D. Jackson, P. D. Miller, W. K. Boyd, F. W. Funk, Authors)

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A mechanism for the LOX-titanium reaction was proposed during a previous investigation (ADD TR 60-258). It was postulated that the impact of a titanium surface immersed in LOX generates sufficient heat to gasify a pocket of oxygen. In addition, the impact tends to compress the oxygen at the local impact sites. A rapid reaction occurs at the fresh surface formed by the impact. The present investigation has established that a fresh titanium

(over)

UNCLASSIFIED

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2. Titanium - Oxidation
3. Titanium - Sensitivity
4. Oxygen (liquid) - Chemical reactions

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surface, formed by rupture of a tensile specimen, would react in gaseous oxygen under approximately 100 psig pressure at temperatures as low as about -250 F. These results tend to substantiate the proposed mechanism.

Means of eliminating or minimizing the reaction of titanium when ruptured in gaseous oxygen were investigated. The addition of HF as a gas to the oxygen resulted in some inhibition. Argon reduced the reactivity of oxygen gas by dilution. Coating the tensile specimens with fluoride-phosphate or with vapor-deposited aluminum did not affect the reactivity. These same coatings furnished some protection to titanium from reactivity during impact under LOX.

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FOREWORD

This summary report was prepared by Battelle Memorial Institute under USAF Contract AF 33(616)-7595. The contract was initiated under Project No. 7351, "Metallic Materials", Task No. 73521, "Behavior of Metals". The work was administered under the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Mr. A. W. Brisbane acting as project engineer.

This report covers the research period from October 1, 1960 to September 1, 1961.

ABSTRACT

A mechanism for the LOX-titanium reaction was proposed during a previous investigation (WADD TR 60-258). It was postulated that the impact of a titanium surface immersed in LOX generates sufficient heat to gasify a pocket of oxygen. In addition, the impact tends to compress the oxygen at the local impact sites. A rapid reaction occurs at the fresh surface formed by the impact.

The present investigation has established that a fresh titanium surface, formed by rupture of a tensile specimen, would react in gaseous oxygen under approximately 100 psig pressure at temperatures as low as about -250 F. These results tend to substantiate the proposed mechanism.

Means of eliminating or minimizing the reaction of titanium when ruptured in gaseous oxygen were investigated. The addition of HF as a gas to the oxygen resulted in some inhibition. Argon reduced the reactivity of oxygen gas by dilution. Coating the tensile specimens with fluoride-phosphate or with vapor-deposited aluminum did not affect the reactivity. These same coatings furnished some protection to titanium from reactivity during impact under LOX.

PUBLICATION REVIEW

This report has been revised and is approved.

FOR THE COMMANDER:

W. J. TRAPP
Chief, Strength & Dynamics Branch
Metals & Ceramics Laboratory
Directorate of Materials & Processes

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

Considerable interest has been shown in the use of titanium as a material of construction by the missile industry. Titanium has low density; it is strong and corrosion resistant. These properties make it an attractive candidate material for the construction of tankage for rocket fuels and oxidizers.

In February, 1959, the first indication of titanium sensitivity to liquid oxygen (LOX) was reported. A number of companies began testing the impact sensitivity of titanium at that time. There was considerable scatter in the results and some confusion in their interpretation. In order to clarify the situation, a basic study, aimed at determining the primary factors involved in the reaction between titanium and LOX, was commenced in May, 1959, by Battelle Memorial Institute under sponsorship of Wright Air Development Center (now Aeronautical Systems Division), Wright-Patterson Air Force Base, Ohio.

The Summary Report (WADD TR 60-258), issued in March, 1960, gave the results of (1) a literature survey and (2) the experimental program. The literature review indicated that titanium was impact sensitive in LOX below the limit considered acceptable for other metals found satisfactory in LOX service. The experimental program covered an investigation of several factors, singly and in a controlled manner:

(1) Exposure of a fresh surface of titanium immersed in LOX, by rupture and by tearing

(2) Deformation of the surface by impact, using steel balls

(3) Impact of smooth, specially cleaned, flat surfaces

(4) Variation in LOX pressure and the velocity of LOX over the titanium surface.

(5) Galling of the surface under LOX.

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None of these factors per se was found to be the primary cause of the reaction. The mechanism proposed was that the heat generated by impact produces a pocket of gaseous oxygen in the LOX. This trapped gas is compressed at the point of impact. The fresh surface exposed by the impact tends to react with the high-pressure oxygen gas present. Propagation is dependent on the balance between the amount of heat generated and the rate of heat loss from the site of the reaction.

The present investigation was initiated to define more closely the mechanism of the titanium-LOX reaction. Particular emphasis was placed on establishing whether reactions could occur between titanium and gaseous oxygen at low temperatures approaching that of LOX under a wide range of conditions.

A second major phase of study was directed toward investigating possible methods for inhibiting the oxygen-titanium reaction.

This present report summarizes the experimental program carried out at Battelle Memorial Institute from October 1, 1960, to September 1, 1961.

SUMMARY

The reactivity of a freshly formed titanium surface has been investigated in high-pressure gaseous oxygen over a range of temperatures from that of LOX to room temperature. The oxygen atmosphere was maintained at the desired pressure in a specially fitted autoclave. A fresh surface was exposed to the oxygen by breaking a titanium tensile specimen in situ.

Unalloyed titanium (Ti-75A) and Ti-6Al-4V alloy were consumed by violent reactions when ruptured in gaseous oxygen under suitable pressure at from -190 F to room temperature. The threshold pressure for the propagating reactions was found to be extremely low. An oxygen pressure of only 100 psig was sufficient to ignite Ti-75A at -190 F, and only 75 psig was needed at room temperature. The Ti-6Al-4V alloy was slightly less reactive and required 125 psig at -190 F and 100 psig oxygen at room temperature.

The results from the experimental program continue to support the hypothesis for the mechanism of the reaction of titanium impacted in LOX. It has been shown that reactions will occur at freshly formed titanium surfaces in gaseous oxygen under pressure over a wide temperature range down to near LOX temperatures. Apparently, the fresh surface is essential for the reaction. Other investigators have shown that titanium will not ignite in high-pressure oxygen until the temperature of the metal surface is raised to near the melting point.

A literature survey showed that the impurity content of LOX is very low. Only solid impurities in LOX are believed to affect the impact sensitivity of titanium.

The experimental program included an investigation of means of eliminating or minimizing the reaction of titanium when ruptured in gaseous oxygen. Two means were tried, namely (1) gaseous additions to the oxygen atmosphere and (2) the coating of titanium surfaces. These experiments were conducted under conditions of oxygen pressure at which reactions had occurred previously. It was found that the addition of 2 per cent HF gas to oxygen at room temperature raised the threshold pressure for the reaction from 75 to about 200 psig. An inert gas also reduced the titanium sensitivity by acting as a diluent. However, the addition of about 5 per cent or more of argon was required to raise the threshold to about 200 psig. Fluorine additions apparently increased the reactivity of the fresh titanium surface.

Coated titanium tensile specimens were ruptured in gaseous oxygen at room temperature. No reduction in reactivity was noted when using coatings of a fluoride-phosphate or a vapor-deposited aluminum. In fact, the experiments indicated that somewhat greater damage occurred with an aluminum coating than with uncoated specimens.

Impact studies showed some effectiveness for the fluoride-phosphate and vapor-deposited aluminum coatings for inhibiting reactions in LOX, particularly for 75A material.

EXPERIMENTAL PROGRAM

Tensile Rupture of Titanium in High-Pressure Oxygen

The following paragraphs describe an experimental program which was designed to investigate the reactivity of a fresh titanium surface in gaseous oxygen over a wide range of temperatures. The fresh surface was obtained by breaking a titanium tensile specimen, and the atmosphere was maintained in a specially outfitted autoclave system.

Equipment and Operation

A standard 1-liter AISI Type 316 stainless steel autoclave was used as the container. It was fitted with a holder so that a tensile specimen could be fractured while being exposed to high-pressure gaseous oxygen at low temperature. Figure 1 is a schematic diagram of the autoclave system used.

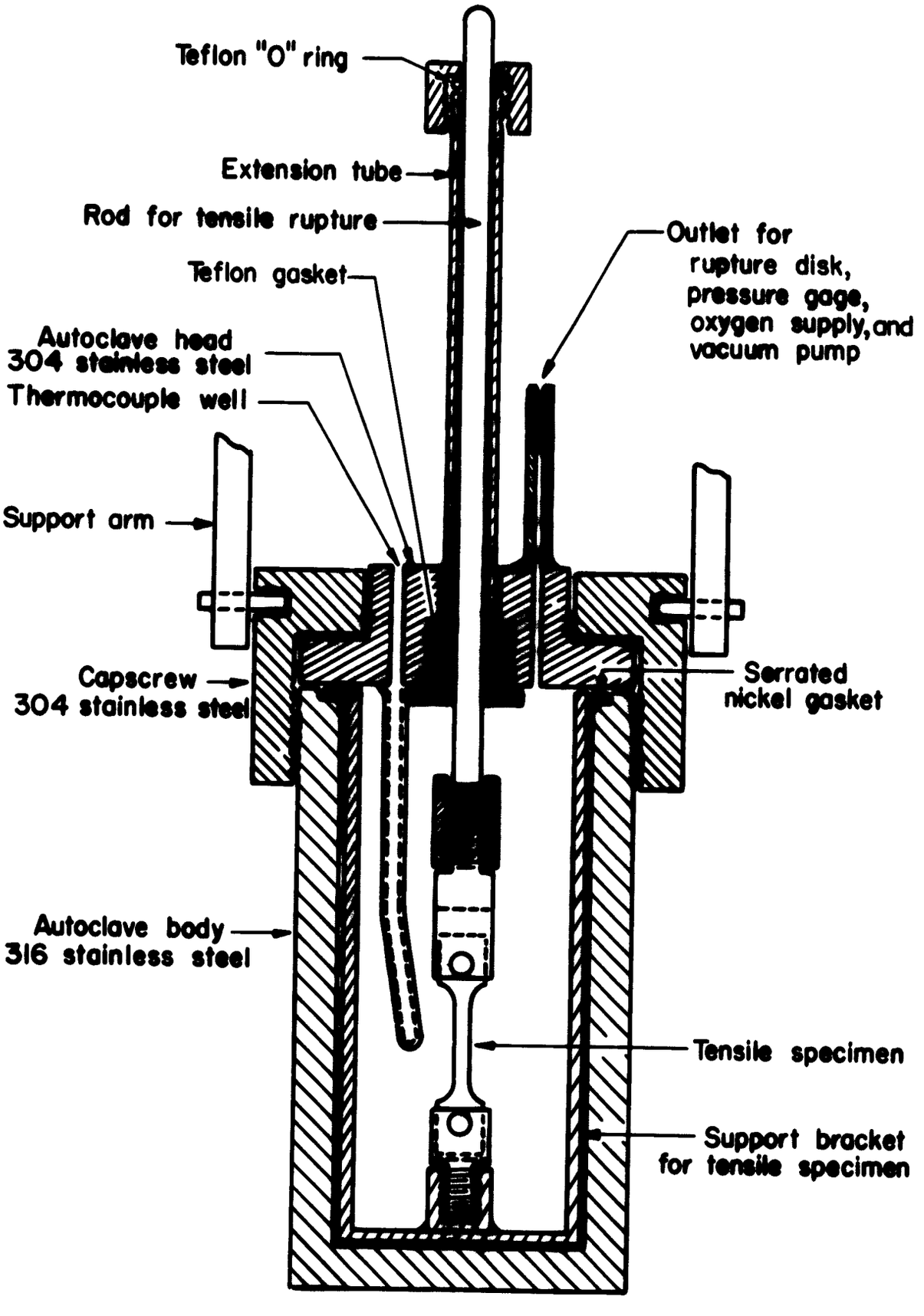

FIGURE 1. SCHEMATIC DIAGRAM OF STRESS-RUPTURE ASSEMBLY

The load was applied to the system from a hydraulic ram connected to the specimen through the pull rod. The relative size and shape of the components are shown in Figure 2.

The top of the specimen was attached to the pull rod and the bottom of the specimen to the stainless steel support bracket by use of stainless steel pins about 0.25 inch in diameter. To protect the autoclave in the event of a violent increase in temperature, a Pyrex cylinder was placed around the specimen within the support bracket, as shown in Figure 2. In later experiments, it became expedient to use a ceramic liner between the walls of the autoclave and the support bracket.

Figure 3 shows the support used for mounting the autoclave and pull jack. The pull rod was sealed at the top of the extension tube with a Teflon O-ring. The autoclave was cooled in a large stainless steel Dewar, shown in the photograph. The temperature was measured with a copper-Constantan thermocouple located about 1 inch from the center of the specimen. Additional thermocouples were attached to the outer autoclave surface at several other areas.

Procedure

Both Ti-75A and Ti-6Al-4V tensile specimens were prepared from sheet stock. The physical properties and the chemical analysis for each alloy is listed in Table 1. The specimens were machined 2-11/16 inch long by 9/16 inch wide with a reduced section 1 inch long by 0.19 inch wide and 0.050 inch thick. The original surface was left in the as-received condition, and the edges were surface ground.

TABLE 1 ANALYSES OF TITANIUM MATERIALS (a)

Specimens were 0.050 inch thick

Physical Analysis					Chemical Analysis, %					
Yield Strength, psi	Tensile Strength, psi	Elongation, per cent	Bend Test (b)	Surface Roughness, microinches	C	Fe	N_2	H_2	Al	V
				Ti-75A, Heat M7826						
L-80,500	100,150	22	2.0T	15-20	.025	0.08	.009	.005	--	--
T-91,600	105,800	21	2.0T	35-40						
				Ti-6Al-4V, Heat M8545						
L-138,300	147,400	14	2 8T	18-20	.020	0.17	.020	.007	6.0	4.1
T-143,700	150,500	15	3.6T	25-30						

(a) Produced by TMCA

(b) Press brake at 105 degrees.

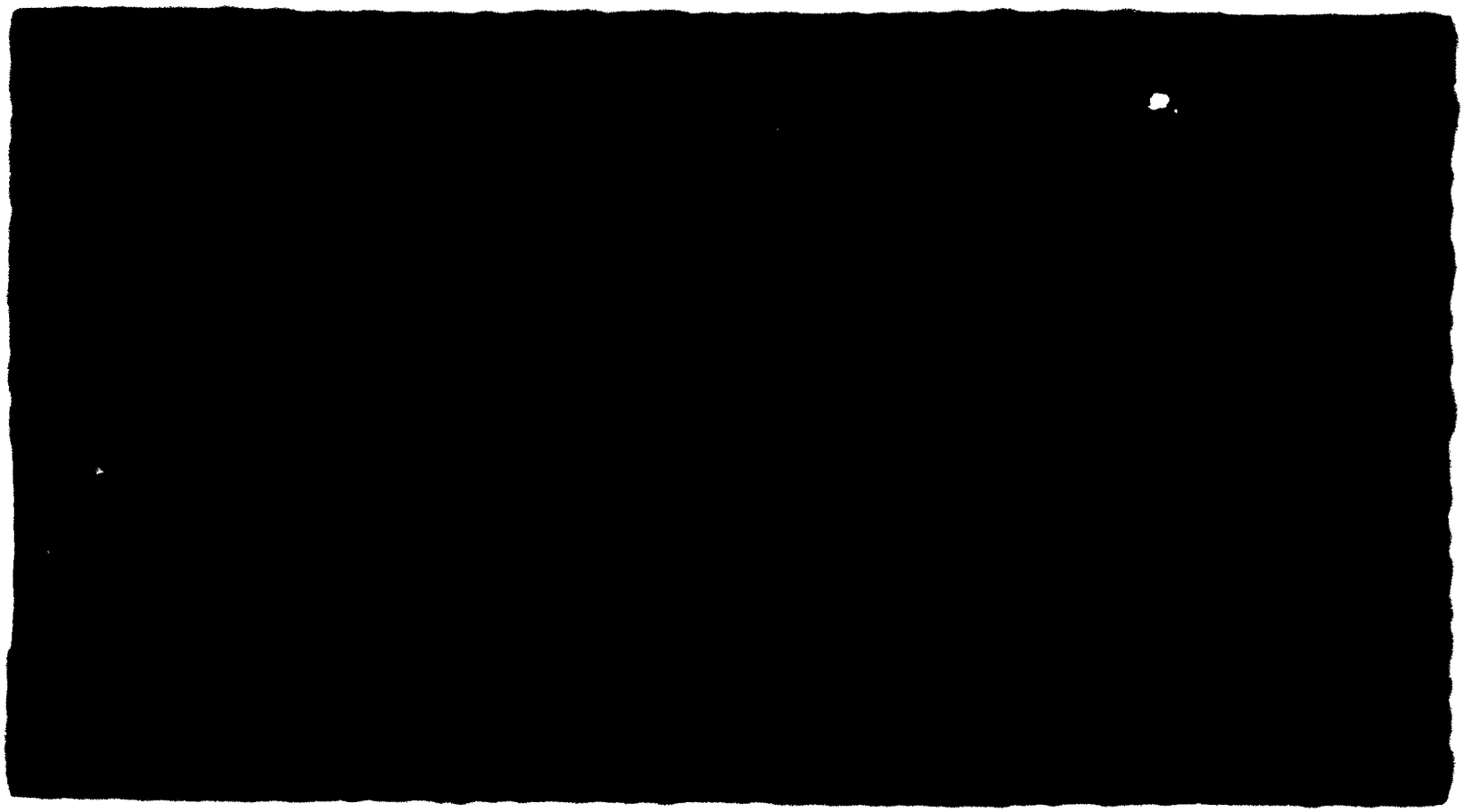

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FIGURE 2. INTERNAL VIEW OF AUTOCLAVE PARTS

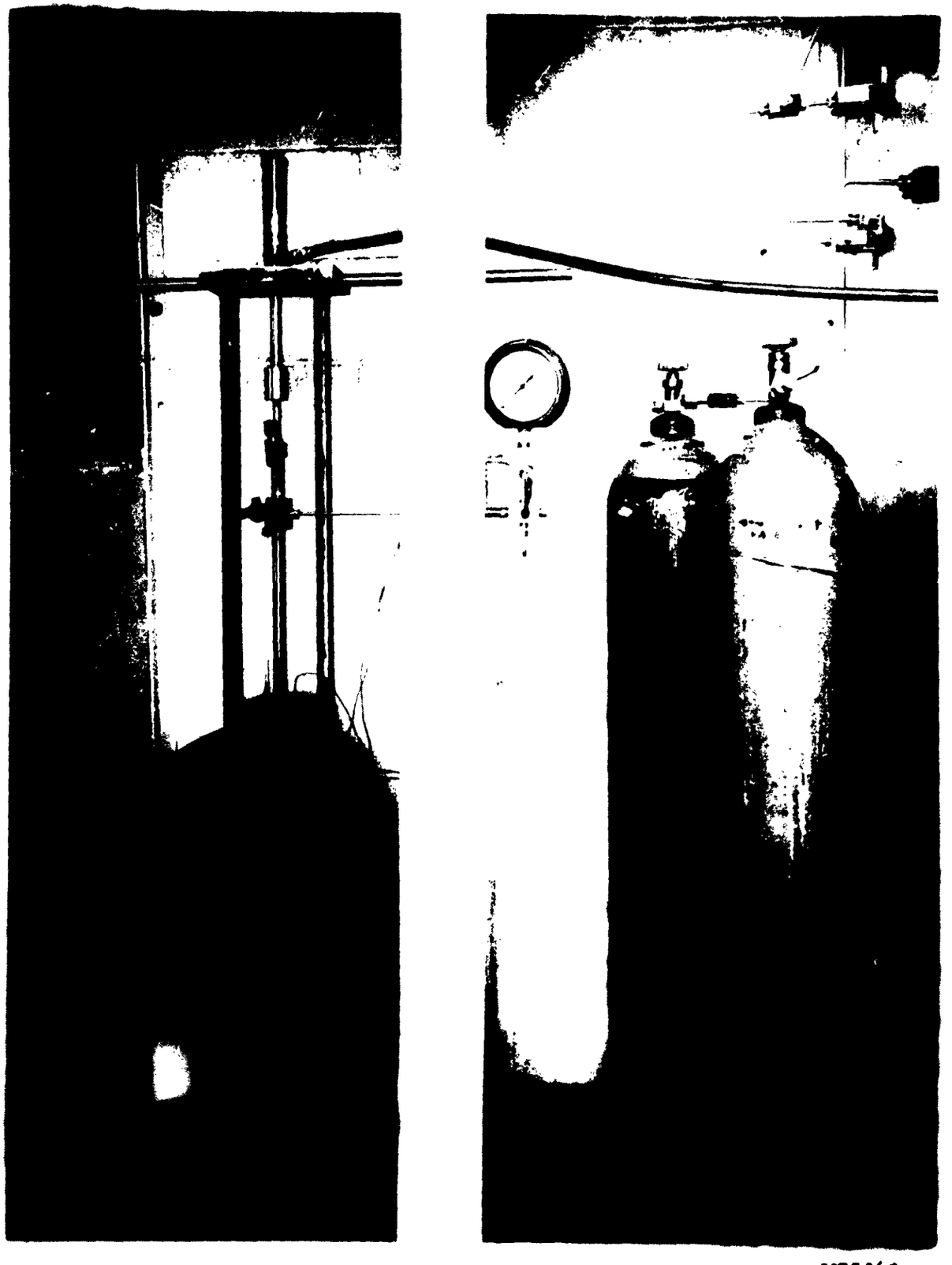

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FIGURE 3. ASSEMBLED AUTOCLAVE IN HIGH-PRESSURE ROOM

All materials used in contact with high-pressure oxygen were cleaned thoroughly by first scrubbing with soap and water, followed by degreasing for 1/2 to 1 hour in a boiling alkaline cleaner*. After rinsing in water and drying, the materials were given a final degreasing for 1/2 to 1 hour in distilled carbon tetrachloride. After cleaning, these materials were handled only by clean metal tools.

In the conduct of an experiment, a standard sheet tensile specimen was first fastened in place using stainless steel pins. Next, the specimen assembly was inserted into the autoclave and sealed. The hydraulic jack assembly was then fastened in place (see Figure 3).

In the early experiments, the system was leak tested by adding high-pressure helium. If no significant pressure drop occurred, the pressure was released. The system was evacuated by a vacuum pump and flushed with helium two to three times. After the final evacuation, the system was pressurized with gaseous oxygen.

In later experiments, the atmosphere was obtained by repeated flushing with oxygen under pressure. This modification avoided the possibility of nitrogen from the air leaking into the system during the evacuation cycle. The final pressure adjustment was made when the autoclave had been cooled to the desired temperature.

The autoclave was cooled in a stainless steel Dewar by using liquid nitrogen. The liquid level was adjusted to 2 to 3 inches above the bottom of the autoclave. The upper portion of the autoclave remained in the cold nitrogen-vapor phase. The top of the Dewar was closed with a thick Styrofoam insulating cover. The temperature in the vapor phase of the Dewar was controlled with tank nitrogen gas and a circulating fan. When the temperature, measured inside the autoclave near the specimen, was close to the desired value, the Dewar was lowered so that the autoclave was completely in the vapor phase.

Then, the oxygen pressure was adjusted to the desired level and the system was allowed to reach an equilibrium temperature. The specimen was ruptured by pumping the hydraulic system. The force required to break the specimen was indicated by the recording needle on the hydraulic system gage.

The temperature, indicated by the thermocouple in the well near the specimen, was registered on a fast-response recorder. The system pressure was observed on the pressure gage by use of a mirror. A reaction was indicated by an immediate temperature rise and possibly a change in pressure. Experience showed that it was desirable to release the oxygen pressure, usually within 10 to 30 seconds after rupture. This stopped the burning-titanium reaction, and thus prevented serious damage to the stainless steel autoclave fittings.

*The alkaline cleaner consisted of 30 g/l sodium metasilicate, 7.5 g/l sodium hydroxide, and 0.5 g/l Duponol.

Rupture of Unalloyed Titanium

Tensile specimens of Ti-75A were ruptured in gaseous oxygen at -250 F, -190 F, -50 F, and room temperature. It was anticipated that pressures of the order of several hundred pounds per square inch might be required to initiate the reaction. However, as shown by Table 2, oxygen pressures of the order of only 100 psig were sufficient, except at -250 F, to ignite the titanium.

Reactivity at -250 F. At -250 F, no reaction was obtained at an oxygen pressure of 100 psig, and the fracture face was bright and metallic. No higher pressure could be used since gaseous oxygen condenses at this temperature at slightly above 100 psig.

Reactivity at -190 F. At -190 F, reactions were obtained at pressures as low as 100 psig, whereas no indication of any reaction was seen at 75 or 50 psig. The reactions obtained at the higher pressures (550 and 450 psig) were very violent. The temperature in the thermocouple well, which was about 1 inch away from the specimen, rose to nearly room temperature in Experiment 2 and rose to above 600 F in Experiment 3. These reactions resulted in complete burning of the titanium specimen and partial burning of the specimen grip, as shown in Figure 4. Note that nearly 1/2 inch of metal was removed from this grip. The molten metal caused the stainless steel support bracket to be welded to the autoclave bottom in Experiments 2 and 3, as shown in Figure 5. Apparently the temperature rise resulting from the burning of the titanium allowed some of the stainless steel parts to melt and ignite in the high-pressure oxygen. From a heat balance of Experiment 3, it was calculated that only about 5 per cent of this heat was generated by the reaction of the 3-gram titanium specimen, and that about 100 grams of stainless steel must have been consumed. For this reason, the oxygen pressure was released in subsequent experiments shortly after a titanium specimen was ruptured. For additional protection to the autoclave, a ceramic liner was placed between the wall and the support bracket.

At lower pressures, down to 100 psig, the damage from the reaction between titanium and oxygen was less severe. In some cases, a portion of the titanium specimen remained, probably because the pressure was released and the oxygen was depleted. Figure 6 shows representative specimen pieces.

At pressures of 75 and 50 psig, at -190 F, no reactions were obtained, and the specimens appeared bright and metallic after rupture. These results show that a threshold pressure of between 75 and 100 psig is required to initiate a reaction at -190 F.

TABLE 2. RESULTS OF TENSILE-RUPTURE EXPERIMENTS IN GASEOUS OXYGEN WITH UNALLOYED TITANIUM (Ti-75A)

Experiment	Temperature, F	Initial Pressure, psig	Oxygen Concentration, g/cc	Final[a] Pressure, psig	Reaction ?	Remarks
1	-250	100	0.031	80	No	Pressure drop due to ram movement
2	-190	550	0.162	>2000[b]	Yes	Rupture disk blew; autoclave damaged
3[c]	-190	450	0.116	655	Yes	Specimen grips ignited; severe autoclave damage
4[c]	-190	250	0.055	325	Yes	Moderate damage to specimen grips
5	-190	150	0.032	150	Yes	Moderate damage to specimen grips
6[c]	-190	100	0.022	100	Yes	Portions of titanium specimen remain[d]
20	-190	75	0.016	75	No	Bright metallic surface at fracture
7[c]	-190	50	0.012	50	No	Bright metallic surface at fracture
24	-50	100	0.014	100	Yes	Severe damage to specimen grips
25	-50	75	0.011	75	Yes	Small piece of titanium specimen remains
26	-50	50	0.008	50	No	Bright metallic surface at fracture
8[c]	77	350	0.033	275	Yes	Severe damage to specimen grips
9[c]	78	150	0.015	150	Yes	Moderate damage to specimen grips; some of titanium specimen remains[d]
12	79	100	0.010	75	Yes	Small piece of titanium specimen remains; grips damaged
18	76	100	0.010	100	Yes	Large piece of titanium specimen remains
13	83	75	0.008	65	Yes	Upper half of specimen showed no reaction
14	80	75	0.008	70	Yes	Large pieces of titanium specimen remain
16	78	60	0.007	60	No	Very small burned spot on fractured face
15	77	50	0.006	50	No	Bright metallic surface at fracture

(a) Oxygen pressure released 10 to 30 seconds after rupture in all experiments except 1, 2, and 3.
(b) LOX may have been condensed during cooling. Rapid evaporation may have produced the pressure rise.
(c) Stainless steel pins brazed in titanium specimens.
(d) See Figure 6.

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FIGURE 4. UPPER STAINLESS STEEL SPECIMEN GRIP, SHOWING DAMAGE FROM TITANIUM-OXYGEN REACTION AT -190 F AND 550 PSIG

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FIGURE 5. REACTION PRODUCTS ON BOTTOM OF AUTOCLAVE LINER, AFTER RUPTURE OF Ti-75A AT -190 F AND 550-PSIG OXYGEN PRESSURE

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Experiment 6	Experiment 9	Experiment 10
Ti-75A	Ti-75A	Ti-6Al-4V
-190 F	Room temperature	Room temperature
100 psig	150 psig	150 psig

FIGURE 6. PORTION OF TITANIUM SPECIMENS REMAINING AFTER REACTION IN HIGH-PRESSURE OXYGEN

Reactivity at -50 F and at Room Temperature. Reactions were obtained at both -50 F and at room temperature for oxygen pressures of 75 psig and above. In Experiment 13 conducted at room temperature, however, only one-half of the specimen burned.

In Experiment 16 conducted at room temperature at 60 psig, no propagating reaction was obtained. However, one very small burned spot was found on the fractured face upon examination (see Figure 7). This shows that the reaction initiated but did not propagate, and apparently represents a borderline case for propagation.

With a pressure of 50 psig, at both -50 F and room temperature, no indication of any reaction was observed. Thus the threshold pressure is between 50 and 75 psig at both these temperatures.

Rupture of Alloyed Titanium

Tensile specimens of Ti-6Al-4V were ruptured in gaseous oxygen at -190 F and at room temperature using the same techniques as for the unalloyed titanium experiments. The results are given in Table 3.

TABLE 3. RESULTS OF TENSILE RUPTURE EXPERIMENTS IN GASEOUS OXYGEN WITH ALLOYED TITANIUM (Ti-6Al-4V)

Experiment	Temperature, F	Initial Pressure, psig	Oxygen Concentration, g/cc	Final[a] Pressure, psig	Reaction?	Remarks
30	-190	125	0.026	115	yes	Specimen largely consumed; grips damaged
29	-190	100	0.022	--	No	Bright metallic surface at fracture
10[b]	75	150	0.015	150	yes	Some of titanium specimen remains; grips damaged[c]
28	79	100	0.010	100	yes	Specimen largely consumed; grips damaged
27	77	75	0.008	75	no	Bright metallic surface at fracture
11[b]	80	75	0.008	75	no	Bright metallic surface at fracture

(a) Oxygen pressure released 10 to 30 seconds after rupture.
(b) Stainless steel pins brazed in titanium specimens.
(c) See Figure 6.

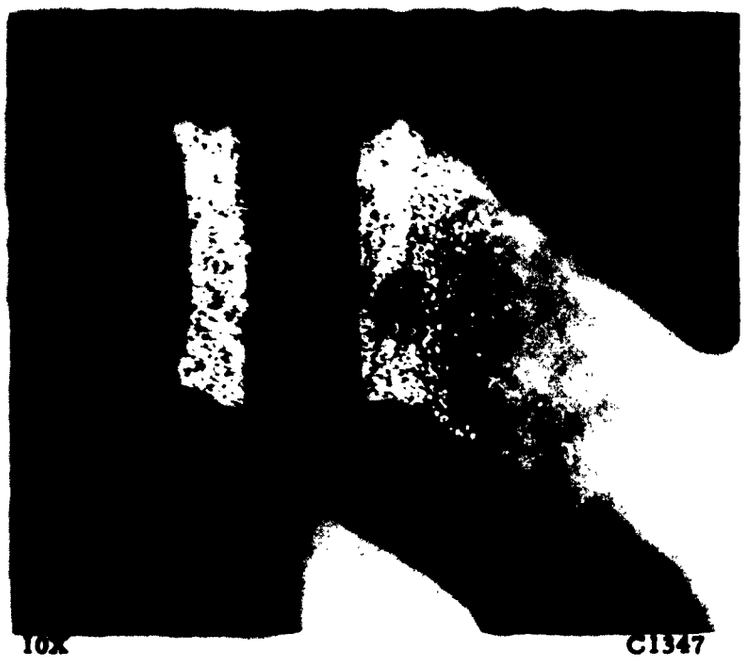

FIGURE 7. TITANIUM TENSILE SPECIMEN RUPTURED AT ROOM TEMPERATURE IN 60-PSIG OXYGEN

Note dark, fused area where reaction initiated but did not propagate. Specimen is from Experiment 16.

Reactivity at -190 F. Reaction of the ruptured titanium specimen was obtained at 125 psig oxygen pressure, but not at 100 psig. This indicates that the threshold pressure is between 100 and 125 psig, which is about 25 psig higher than was obtained for Ti-75A at this temperature.

Reactivity at Room Temperature. Reactions with the alloy were obtained at pressures of 100 and 150 psig. No reaction was obtained in duplicate experiments at 75 psig. Thus, at room temperature, the threshold pressure is lower than at -190 F, being between 75 and 100 psig. This reaction also represents a threshold pressure about 25 psig greater than that for the unalloyed titanium at room temperature.

Threshold Pressure for Reactions

Research under the present contract has shown that, at high oxygen pressures, reactions can be expected when titanium specimens are ruptured over a wide range of temperatures. The data have been summarized in Figure 8, where unalloyed titanium (Ti-75A) is represented by circles, the alloy (Ti-6Al-4V) by squares, and reactions by closed symbols. The lines marked Ti-75A and Ti-6Al-4V are used to separate areas where reactions would be expected from areas where no reactions would be expected, within the limits of experimental error.

The data indicate that probability plays an important role in the reaction. A reaction may initiate but not propagate, as shown by the spot on the fracture face in Figure 7. Or one-half of a broken specimen may burn while no reaction will be found on the other half, as shown by Experiment 13 in Table 2. A threshold pressure is represented by a point on a line in Figure 8. In the area just above a line, it is probable that a reaction will occur. At higher pressures, the reaction is almost certain. Below a line, low probability for a reaction exists and at very low pressures no reaction would be expected.

The threshold line for Ti-6Al-4V is drawn slightly above the line for Ti-75A, indicating that the alloy is less reactive in oxygen than is the unalloyed titanium. These results are unexpected, since previous experience indicated that alloys are slightly more sensitive to reaction under impact in LOX. Since it has been postulated that propagation occurs by dissolution of the titanium oxide in the molten metal, it may be that the alloy is less susceptible to reaction because some insoluble aluminum and vanadium oxides are found at the surface. Further experiments would be required to define the significance of alloy composition on the reactivity. However, the important result is that both Ti-75A and Ti-6Al-4V are quite reactive when ruptured in high-pressure gaseous oxygen.

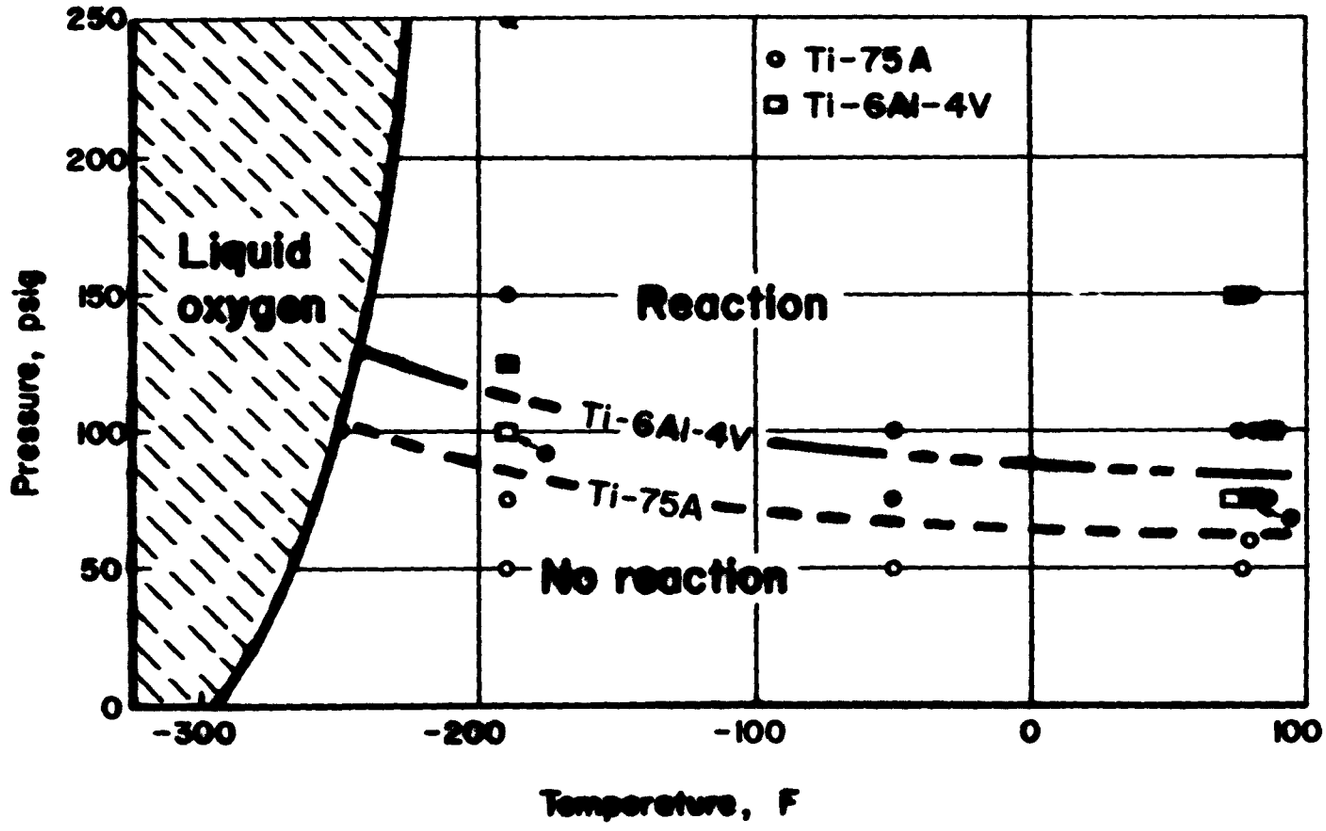

FIGURE 8. REACTIVITY OF TITANIUM RUPTURED IN GASEOUS OXYGEN

Discussion of Mechanism

According to the mechanism postulated in the earlier report (WADD TR 60-258), the reaction between titanium and LOX required the application of several factors in a proper sequence.

First, it was suggested that the reaction did not take place between liquid oxygen and titanium, but that gaseous oxygen was required. The gaseous oxygen was formed at hot spots generated when surface imperfections, chips of metal, or pieces of dirt were impacted.

Second, the gaseous oxygen must touch a fresh titanium surface. Mechanical deformation and rupture during impact would form the active surfaces needed. In addition, the high solubility of titanium oxide in molten titanium enhances the formation of a fresh surface.

Third, portions of the gaseous oxygen trapped in small crevices would be compressed by the force of impact.

The propagation of the reaction is dependent on the amount of heat generated. If more heat is generated than is lost to the surroundings, the process is self-sustaining.

Since the present study has shown that reactions can be anticipated in gaseous oxygen at relatively low pressures near LOX temperatures, the mechanism postulation outlined above has been strengthened considerably.

Various factors related to the reaction mechanism and to the interpretation of the experimental results are discussed in detail in the sections which follow.

Reaction at Fresh Surface. It should be noted that several experiments were conducted to demonstrate that the reaction initiated at the freshly ruptured surface of the tensile bar, rather than at the support pins. Several specimens were prepared with support pins brazed into the holes; thus, any impact during recoil at the instant of fracture was eliminated. These specimens are pointed out individually in Tables 2 and 3. It was found, in the cases where reactions occurred with brazed-pin specimens, that the pin areas were largely undamaged, while the titanium at some distance from the pin had been melted or completely consumed. The appearance of such areas is illustrated quite well in Figure 6. It can be seen that the burned areas are not immediately adjacent to the pin holes.

In other experiments in which unbrazed pins were used, some of the titanium specimen around the pin hole remained intact after reaction, as in Experiments 14 and 18, indicating that the reaction was not initiated at that area.

In Experiment 16, a reaction actually had initiated at the fresh surface, without propagation (see Figure 7). No evidence of any reaction was detected at the pin hole.

Further evidence of the initiation of the reaction at the ruptured surface is furnished by the investigation of Littman and Church.[1] Those investigators showed photographically that the burning reaction propagated from the fractured area at room temperature and above.

Effect of Oxygen Pressure. The relatively flat curves in Figure 8, which separate areas of reaction from those of no reaction, are somewhat unexpected. A more noticeable effect might have been anticipated, particularly since a temperature change of about 2-1/2 times is involved. It is believed that the increased concentration at the low temperatures causes the effect noted. As shown in Table 4, the concentration of oxygen changes considerably as the temperature varies. These values are averages taken between the points of reaction and no reaction, as given in Tables 2 and 3. Over the temperature range used in the present work, this represents a fourfold change in oxygen concentration.

TABLE 4. COMPARISON OF THRESHOLD PRESSURE AND CONCENTRATION FOR REACTION BETWEEN TITANIUM AND OXYGEN

Temperature, F	Ti-75A		Ti-6Al-4V	
	Pressure, psig	Concentration, g/cc	Pressure, psig	Concentration, g/cc
80	63	0.007	88	0.009
-50	63	0.009		
-190	88	0.019	113	0.024
-250	>100	>0.031		

The explanation is that, as the temperature is lowered, the kinetic energy of the molecules decreases and a higher concentration of molecules is required to initiate a propagating reaction. Thus, the temperature and concentration offset one another, and the oxygen pressure, fortuitously, is nearly constant under the experimental conditions used. Further investigation of this point would require the study of the kinetics of the reaction as a function of temperature.

Generation of Heat. One factor, which should be considered in the discussion of the mechanism, is whether the generation of heat is sufficient to initiate the propagating reaction without the exposure of a fresh surface. The temperature of the surface may be raised, as during impact, to some point where rapid oxidation and subsequent burning will occur without necessarily rupturing the surface, as proposed in the hypothesis.

Dean and Thompson[2] reported that titanium was the most reactive material, in high-pressure atmospheres, of the common metals and alloys. It was shown that titanium tubing (about 0.5-inch OD x 0.03-inch wall) would react at 35-psig oxygen pressure when the specimen was heated electrically (within 1 to 2 minutes) to 2400 F. At 285-psig oxygen pressure, reaction occurred at 1600 F. In addition, titanium reacted in a 50 per cent O_2-50 per cent CO_2 mixture, at a temperature of 1400 F, under 285-psig pressure. In 100 per cent CO_2, reaction occurred at 2600 F at 285 psig.

On the basis of the results of these tests, it would appear that titanium heated in LOX at atmospheric pressure would not react until temperatures in excess of 2400 F were obtained over some large area. At these temperatures, rapid diffusion of the oxide coating into the metal would occur, and a fresh surface could actually be formed to initiate the reaction. However, no evidence, such as oxidized or discolored surfaces, has been found to indicate that temperatures in this range can be achieved by impact alone. In addition, the low temperature of the system and vaporization of LOX would tend to remove the heat rapidly.

The experimental results show that a titanium specimen, even when at low temperature, will ignite under pressure if a fresh surface is presented by fracture. According to the hypothesis prepared, the temperature of gaseous oxygen needs only to be high enough so that it will not be condensed when the pressure reaches about 100 psig. This temperature is about -250 F, as shown by the threshold-pressure graph of Figure 8.

It should also be mentioned that the driving force for the reaction is actually greater at low temperature than at room temperature, as shown by thermodynamic considerations. The difference in the free-energy values is only about 5 per cent however; so the effect probably could not be detected. Therefore, the reaction is, essentially, as probable thermodynamically at room temperature or above as at low temperatures, as demonstrated by the experimental results.

Effect of Strain Rate. Previous tensile-rupture experiments, using titanium specimens submerged in LOX, showed that no reactivity at the break was obtained at strain rates from 100 to 10,000 inches per inch per minute. In the present investigation, reactions were obtained under high-pressure gaseous oxygen at a strain rate of about 2 inches per inch per minute. The

strain was produced by constantly pumping the hydraulic system by hand. Since this hydraulic system cannot be controlled as precisely as a standard Universal testing machine, the strain rate during yield probably increases somewhat.

The generation of heat in the sample is believed to be an important factor in the propagation of the burning reaction. Heat is generated during yield by the slip of planes of atoms over one another, and at the moment of rupture when temperatures of the order of the melting point are theoretically possible. These temperatures are highly localized and transient. It is thought that the temperature generated by yield is probably a function of strain rate, whereas the temperature generated at the ruptured surface is always near the melting point. Therefore, it was predicted that, if the specimen were stressed slowly enough, the heat produced during yield would be dissipated away from the rupture zone and the heat balance could be changed enough so that the reaction would not initiate.

Duplicate experiments were performed on specimens of Ti-75A at very low strain rates under 75 psig pressure, and it was found that no reaction occurred. No measure of strain rate is provided for in the equipment; however, it is believed that these rates were at least an order of magnitude lower than the normal pull rate. It was concluded that strain rate was possibly of importance in the titanium-oxygen reaction mechanism, within the limits of experimental error. However, it must be recognized that some probability exists that no reaction would occur even at the normal strain rate. Additional experiments at higher oxygen pressure would be required before any definite conclusion can be reached.

Effect of Impurities. An investigation was made into the impurties generally found in LOX, because of the possibility that some constituent might affect the reactivity of titanium in LOX.

It was found that there are three main types of impurities[3]:

(1) Inert gases, such as nitrogen and argon, which make up most of the impurities in 99.5% O_2.

(2) Hydrocarbons, such as acetylene (maximum permissible level, 2.0 ppm; total permissible hydrocarbon level, 500 ppm)

(3) Other contaminates which generally are solids, such as dirt or water and CO_2, which have low solubility (nil and 5 to 6 ppm, respectively).

Kircher and associates[4] report that LOX used for breathing contains argon as the principal impurity in amounts up to 0.33 volume per cent. The other impurities are:

Nitrogen	20-300 ppm
Carbon dioxide	5-15 ppm
Water	<24 ppm
Helium	<1 ppm
Neon	<1 ppm
Krypton	<5 ppm
Xenon	<1 ppm

Of these impurities, it appears that the solid ones would be most likely to increase the sensitivity of titanium to impact in LOX. These solids also are harmful in other ways, such as plugged filters and valves and eroded pipelines. Special LOX-handling techniques are being put into practice to control these difficulties. Also it has been established that titanium is susceptible to increased reactivity when impacted in the presence of particles, such as Al_2O_3.

Prevention of Titanium Reactions

After demonstrating that titanium is highly reactive when ruptured in gaseous oxygen at pressures as low as 75 psig, attention then was turned to an investigation of ways of eliminating or reducing the intensity of the reaction. This program included two methods of approach: (1) gaseous additions were made to the oxygen atmosphere and (2) coatings were applied to titanium specimens.

These two methods were evaluated by rupturing Ti-75A tensile specimens in the high-pressure autoclave. The experiments were conducted under conditions previously known to cause sustained burning of titanium. Thus, the absence of burning could be taken as an indication of the inhibitive properties of each additive or coating. The operating conditions were 200-psig oxygen pressure at room temperature.

In addition, an evaluation of coatings was made using a drop-weight impact test.

Inhibition by Gaseous Additions

Several requirements must be considered in the study of inhibitors for use in LOX:

(1) Only small quantities of the additive must be required, so as not to impair the oxidizing properties of LOX.

(2) The quantity and function of the inhibitor should be such as to allow a passive barrier to form rapidly on the fresh titanium surface at the time of rupture.

(3) The additive should not be reactive with LOX. For example, organic-type corrosion inhibitors cannot be considered because of their reactivity in contact with LOX.

(4) The additive selection is limited to materials with some solubility at the low temperatures associated with LOX.

It is believed that chemicals that provide a fluoride film would satisfy many of these requirements. For example, although titanium is impact sensitive in liquid fluorine, propagation does not occur as it does in LOX. Accordingly, additions of hydrogen fluoride and of fluorine were considered attractive possibilities for investigation.

Before a given concentration of hydrogen fluoride or fluorine was added to the LOX, the internal surfaces of the autoclave and the internal parts were passivated by slowly circulating an inert gas containing some of the inhibitor. A 1/2-hour exposure was used for hydrogen fluoride and a 1-1/2-hour exposure when fluorine was the inhibitor. This was done to form a protective film on the surface and to prevent depletion of the inhibitor in the LOX during the experiment. In the case of fluorine, if the vessel was not first passivated, there would be danger of rapid oxidation of any surface contamination which might remain after cleaning. In some experiments, the autoclave was allowed to stand overnight with the inhibitor present under static conditions. After passivation, a mixture of oxygen and inhibitor was metered into the autoclave at atmospheric pressure. This mixture was controlled so that the desired concentration of inhibitor would be present when the system was pressurized with oxygen.

Hydrogen Fluoride. Hydrogen fluoride at two concentrations was added to the oxygen. The results of the stress-rupture experiments are listed in Table 5. It can be seen that, with a 5 per cent HF addition, no reaction was obtained at either 100- or 200-psig total pressure. When the amount of HF was lowered to 2 per cent, no reaction was obtained in two out of three experiments at 200 psig. Since reactions would be expected in pure oxygen at 200 psig, it was concluded that a 2 per cent HF addition produced some inhibition and that a 5 per cent HF addition resulted in a higher order of inhibition.

Fluorine. Elemental fluorine, in amounts ranging from 2 to 5 per cent, was added to gaseous oxygen at 200 psig. The results in Table 5 show that the burning reaction of titanium was not inhibited. In fact, in the case of the 5 per cent addition, it appeared that the reaction was enhanced, as evidenced by the severe damage to the specimen grips. Accordingly, further experiments were carried out to obtain a better understanding of the apparent inhibition furnished by hydrogen fluoride; these studies are outlined in the next section.

TABLE 5. RESULTS OF STRESS-RUPTURE STUDIES WITH INHIBITORS IN GASEOUS OXYGEN AT ROOM TEMPERATURE WITH UNALLOYED TITANIUM

Experiment	Addition, per cent	Time of Contact, hr	Total Pressure, psig	Reaction ?	Observations After Rupture
32	5 HF	19	110	No	Thin brown scale on specimen
33	5 HF	19	208	No	Heavy brown scale which appeared moist on specimen
37	2 HF	19	212	No	Thin brown scale on specimen[a]
39	2 HF	20	199	No	Some scale on specimen
38	2 HF	2	208	Yes	Portions of titanium specimen remained; grips damaged
41	5 Fluorine	22	215	Yes	Very severe damage to specimen grips
40	2 Fluorine	6	210	Yes	Upper half of specimen unburned except for one small burned spot
35	5 Argon	--	210	No	Three very small burned spots
36	2 Argon	--	211	Yes	Severe damage to specimen grips

(a) Scale rinsed off easily in water.

Argon (Dilution). It was postulated that the effectiveness of hydrogen fluoride might be related to a dilution effect, rather than to corrosion inhibition by the formation of a film. In order to determine what role dilution of the oxygen by the hydrogen fluoride played in the decreased sensitivity of titanium, argon was substituted for hydrogen fluoride in two experiments. Table 5 shows that a reaction occurred with additions of both 5 and 2 per cent argon. However, in the case of the addition of 5 per cent argon, only a few burned spots could be seen on the titanium pieces where normally the metal is almost completely consumed. Therefore, it appears that the role of hydrogen fluoride may be mostly related to inhibition and partly to dilution of the oxygen.

Protection of Titanium by a Coating

Several experiments were made to study the inhibitive properties of chemical-conversion coatings and metallic coatings on titanium. It was recognized that the coating would not cover the freshly exposed area at a fracture. However, it was thought possible that the coating near the ruptured area might afford some protection from the spread of ignition (1) by providing an inert barrier or (2) by promoting higher rates of heat transfer (as with an aluminum coating) and thereby tending to quench the reaction.

Fluoride-Phosphate Coating. The first type of coating used was a fluoride-phosphate treatment. Originally, this coating was developed to facilitate forming operations with titanium. In wire drawing, for example, titanium tends to gall badly when bare. The specimens were prepared for coating by first degreasing in a boiling alkaline cleaner, pickling in HNO_3-HF solution, and coating in a sodium phosphate-potassium fluoride-hydrogen fluoride bath[5] for 1 to 2 minutes (see tabulation below). The specimens then had a dark gray-brown color.

Pickle Bath	Coating Bath
600 ml H_2O	1000 ml H_2O
352 ml 70% HNO_2	50 g $Na_3PO_4 \cdot 12H_2O$
70 ml 48% HF	8 g $KF \cdot 2H_2O$
	26 ml 48% HF for 75A
	150 ml 48% HF for 6Al-4V

Table 6 shows that very little benefit, if any, was gained from the presence of this coating on Ti-75A tensile specimens. At least, it appears that it is not so effective as hydrogen fluoride gas.

TABLE 6. RESULTS OF STRESS-RUPTURE STUDIES IN GASEOUS OXYGEN AT ROOM TEMPERATURE WITH COATED UNALLOYED TITANIUM

Experiment	Pressure, psig	Reaction?	Observations After Rupture
		Fluoride-Phosphate Coating	
44	200	Yes	Moderate damage to specimen grips
46	100	Yes	Portion of titanium specimen remains; grips severely damaged
43	100	No	Coating thin in elongated section of specimen
		Aluminum Coating	
42	205	Yes	Very severe damage to specimen grips
45	100	Yes	Ditto

Vapor-Deposited Aluminum Coating. Aluminum-coated titanium, Ti-75A, specimens were investigated also. Aluminum has good heat-transfer properties and is considered nonreactive in oxygen. The specimens were gas plated to a thickness of about 0.3 mil by heating to 260 C in an atmosphere of argon and triisobutyl aluminum. (This work was performed by Mr. J. J. Crosby of Aeronautical Systems Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.) The specimens were scrubbed in a soap and water solution prior to rupture in gaseous oxygen. Table 6 shows that no lessening in reactivity was obtained. In fact, more damage occurred than was normally encountered in experiments with uncoated titanium.

Drop-Weight Impact Experiments

Drop-weight impact experiments were used to determine the sensitivity of titanium panels to impact while in LOX.

The machine consists of a 44-pound plummet that drops by free fall on the striker. The bevel-faced striker is a 1/2-inch-diameter rod, 3/4 inch long, which rests directly on the test coupon. The coupon and striker are placed in a tin-plated steel cup which is the LOX receptacle. LOX is added to the cup, to precool the specimen for about 5 minutes before the impact is made.

Reaction is indicated by a bright flash upon impact, or by burned spots observed on the panel after the LOX evaporates and the sample is dried.

The reactivity of titanium panels protected by the fluoride-phosphate coating was compared with that of unprotected panels in the as-received condition. Reactions were found for 7 out of 20 impacts at the 70 foot-pound level for unprotected Ti-75A. No reactions were obtained for nine impacts at 70 foot-pounds for coated Ti-75A. This indicates that protection from reactions resulting from impact might be obtained for titanium by use of a coating.

In the case of the Ti-6Al-4V alloy, not so much protection was obtained with the fluoride-phosphate coating as for Ti-75A. Reactions were observed in one out of three impacts with the coating and in two out of four impacts with unprotected panels at the 70 foot-pound level.

Differences obtained in the thickness of the coating for the two types of titanium specimens may cause the difference in the reactivity. For unalloyed titanium, the bath deposits a heavy gray coating. For the alloyed material, the bath produces a colorless coating which appears to be very thin. It is believed that a thicker coating would offer greater chance for protection.

The present study shows that surface roughness plays an important role in the reactivity of uncoated titanium. Previously, it was found that with smooth (6 to 7 microinches rms) alloy panels, no reactions were obtained out of 11 impacts at 70 foot-pounds. With the as-received panels, 7 out of 20 and 2 out of 4 reactions occurred for unalloyed and alloyed titanium, respectively. The surface roughness of these materials is about 30 to 40 microinches rms as shown in Table 1. Thus, the reactions probably begin at rough areas, where oxygen can be trapped and compressed.

The use of vapor-deposited aluminum coatings of titanium was investigated only briefly. No reaction was obtained with one panel impacted at the 70 foot-pound level.

Evidence was found in the literature that an aluminum coating is now in use for the protection of titanium in LOX. A recent Russian patent[6] states that titanium and titanium alloys are clad with aluminum on both sides to prevent spontaneous ignition when exposed to pressurized LOX.

It was concluded from the impact study that heavy coatings, such as the fluoride-phosphate and vapor-deposited aluminum coating, offer some protection to titanium when impacted under LOX. Additional work would be necessary to evaluate other coatings, such as anodized coatings and thin metal films.

Discussion

On the basis of the experiments described in the preceding sections, it does not appear that a simple solution is available to reduce the sensitivity

of the titanium surface to reactions following rupture in pressurized oxygen. Although hydrogen fluoride gas affords some inhibiting effect, it was not of sufficient magnitude to be practical. For example, it appears that a 2 per cent HF addition raised the threshold pressure of oxygen only from 75 psig to less than 200 psig.

It should be pointed out that the experimental conditions under which the current study was performed are extremely severe. Such conditions were chosen to help elucidate the mechanism of the titanium-LOX reaction in the most straightforward manner. The stress rupture of titanium components in service would seldom be expected. On the other hand, conditions could be visualized where the assembly would be subjected to impact; this condition, however, would be less likely to initiate a reaction. Coatings appear to offer some protection in this case.

CONCLUSIONS

The experimental program had as its two main objectives: (1) a better understanding of the proposed mechanism by investigation of the reactivity of titanium in gaseous oxygen and (2) investigation of means of preventing or minimizing the reaction. On the basis of experimental results, several conclusions can now be reached:

(1) The mechanism postulated for the reaction between titanium and liquid oxygen has been shown to be in agreement with the experimental results. It has been demonstrated that gaseous oxygen under pressure will initiate a propagating reaction when titanium is ruptured. Thus, according to the hypothesis, heat must be generated to gasify the LOX. The reaction then begins at the fresh surface formed by the ruptured tensile specimen. When more heat is produced by the initiation than is lost to the surroundings, the reaction proceeds until one of the reactants is consumed.

(2) The oxygen pressure required for the propagating reaction with titanium is about 100 psig over the temperature range from about -250 F to room temperature.

(3) The alloy Ti-6Al-4V is slightly less reactive than Ti-75A in gaseous oxygen.

(4) Impurity levels found in LOX are very low, and it was not determined what effect these have on reactivity.

(5) Gaseous additions to the oxygen atmosphere can increase the oxygen pressure required for the reaction, thus lowering the sensitivity. The addition of hydrogen fluoride inhibits the reaction slightly, and even argon affords some benefit by dilution. Fluorine gas tends to increase the sensitivity to reaction.

(6) A fluoride-phosphate or aluminum coating on a titanium tensile specimen does not afford protection to a titanium tensile specimen ruptured in gaseous oxygen.

(7) A fluoride-phosphate or aluminum coating on titanium panels affords some protection against impact in LOX.

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